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(54) Title: BLEACHING PULP

(57) Abstract: Pulping liquors used in the bleaching of pulps by hydrogen peroxide, and containing catalase-producing bacteria and/or catalase enzyme are treated with tris (hydroxymethyl) phosphine or a tetrakis (hydroxymethyl) phosphonium salt to kill the bacteria and destroy the enzyme.

BLEACHING PULP

This invention relates to bleaching of pulp by hydrogen peroxide and in particular to a method of treating pulping liquors by preventing or reducing the breakdown of peroxide by catalase.

Catalase is an enzyme that is produced by bacteria commonly found in pulp and paper mills. By consuming hydrogen peroxide, catalase can lower bleaching efficiency and decrease brightness levels of the finished paper.

It is known to kill catalase-producing bacteria by using a biocide such as glutaraldehyde.

The bactericidal efficacy of glutaraldehyde against catalase-producing bacteria present in pulp and water is known from US5728263. To be of use in pulp operations, a biocide must additionally be able to destroy the enzyme chemically.

It has now been found that tris (hydroxymethyl) phosphine and the tetrakis (hydroxymethyl) phosphonium salts (referred to collectively herein as THP) are more effective than glutaraldehyde at killing catalase-producing bacteria.

It has also been found that THP can be used more efficiently than glutaraldehyde to chemically destroy catalase as well as to kill the bacteria that produce it.

The present invention provides a method of treating pulping liquors for use in the bleaching of pulp by hydrogen peroxide, said liquors containing catalase and/or catalase-producing bacteria, with a biocide which reduces

or destroys said catalase and/or said bacteria, characterised in that said biocide comprises tris (hydroxymethyl) phosphine (THP) or a tetrakis (hydroxymethyl) phosphonium salt (THP salt).

Preferably, the THP salt is tetrakis (hydroxymethyl) phosphonium sulphate (THPS).

Alternatively, the THP salt may be tetrakis (hydroxymethyl) phosphonium chloride, phosphate, bromide, carbonate, acetate, citrate, formate, lactate or borate.

The THP or THP salt is preferably added to the pulping liquor at a concentration of from 5 to 1000ppm, desirably 10 to 200ppm, more usually 15 to 100ppm, especially 20 to 50ppm. The pH may be from 4 to 12, usually 5 to 10, eg: 7 to 9 in an alkaline pulping system, or 5 to 7 in an acid pulping system.

The invention is illustrated by way of the following examples:

EXAMPLE 1

- Experiments were carried out using a synthetic solution of catalase.
- The catalase concentration used was ~ 3ppm.
- Solutions were all buffered at pH 8 (the anticipated pH of the stock chest).
- Contact times of 5, 15 and 30 minutes were allowed.
- Experiments were carried out at 20°C and 45°C.
- Nominal biocide concentrations of 100ppm and 600ppm (ai) were used.
- Initial hydrogen peroxide concentration = 0.5 % w/w.

The experiments used a 75% wt on wt solution of tetrakis (hydroxymethyl) phosphonium sulphate, sold commercially under the Registered Trade Mark **TOLCIDE PS75** and a 50% wt on wt solution of glutaraldehyde for comparison.

The principle of the experiments carried out was that when a solution containing active levels of the catalase enzyme is added to hydrogen peroxide, effervescence is observed as the reaction below is followed:-

$$2H_2O_2 \quad + \quad \text{Catalase} \quad \rightarrow \quad O_2 \quad + \quad 2H_2O$$

For the purpose of the experiments solutions of the catalase enzyme were contacted with either 100 or 600ppm (ai) of **TOLCIDE® PS75** or glutaraldehyde for 5, 15 and 30 minute contact times. The catalase/biocide solution was then added to a fixed volume of 0.5 %w/w hydrogen peroxide and allowed to react. The residual concentration of hydrogen peroxide was quantified using a potassium permanganate titration and the % hydrogen peroxide remaining taken as a measure of the success of catalase destruction.

The results obtained are tabulated below in Table 1.

Table 1

Concentration of Biocide/Temperature °C	Contact Time (minutes)	% Hydrogen Peroxide Remaining	
		TOLCIDE® PS75	Glutaraldehyde
600ppm/45°C	5	37	<1
	15	56	3
	30	100	100
100ppm/45°C	5	<1	<1
	15	2	<1
	30	76	37
600ppm/20°C	5	22	<1
	15	49	25
	30	75	60
100ppm/20°C	5	<1	<1
	15	18	16
	30	39	25

In the absence of biocide treatment NO residual hydrogen peroxide was observed in the presence of catalase at a 3ppm level.

The experiments indicate that **TOLCIDE® PS75** is superior to glutaraldehyde for catalase destruction.

EXAMPLE 2

Samples of de-inked pulp and pulper fill water were received from two de-inking plants, samples 1 and 2. Control needs to be maintained over bacterial populations within these systems. Bacterial build-up in the re-cycled alkaline water, and contamination of the recycled fibre cause catalase levels to increase. The catalase breaks down peroxide in the helico pulper and stops the bleaching effect of the peroxide. It also means that maintenance of residual peroxide, which is required in the alkaline loop, is not possible.

Catalase is produced predominantly by general aerobic bacteria (GAB). During respiration, various toxic oxygen derivatives are produced within the bacterial cell, because of this, bacteria produce enzymes to destroy these toxic substances. The most common enzyme in this category is catalase, which breaks down hydrogen peroxide to oxygen and water.

As it is GAB which cause the problems of catalase build-up, quantitative suspension tests (QSTs) were carried out to compare the ability of THPS and glutaraldehyde to reduce the number of GAB present in the pulp/water samples provided.

An initial test was also carried out whereby mixed pulp/water samples, which had already been exposed to various concentrations of the test biocides, then had hydrogen peroxide added to them. The peroxide levels in these samples was monitored over one hour to gain an indication of the levels of catalase present by the rate of breakdown of hydrogen peroxide.

Before carrying out any efficacy tests, material from all of the pulp and water samples provided was plated out onto tryptone soya agar plates and incubated at 45°C, ie: plant operating temperature, for 1-2 days.

This was to ensure that the bacterial populations were similar both in appearance and, in the case of the water samples, in numbers.

All water samples were found to contain high levels of GAB, ie: in the order of 10^7 cfu/ml. (cfu = colony forming units).

It was assumed that the concentration of the pulp samples provided was approximately 15%, therefore a combined pulp/water sample was prepared by diluting sample 1 pulp with sample 2 water at a ratio of 1 in 15 (w/w), thus giving a pulp concentration of approximately 1%, which could be handled relatively easily within these tests. This diluted pulp sample was thoroughly mixed and dispersed in 9.0g amounts into sterile universal bottles. These were then incubated at 45°C for 1 hour.

Immediately prior to beginning the test, stock solutions of **TOLCIDE® PS75** and glutaraldehyde were prepared at the following concentrations in sterile WHO standard hardness water:

500, 1000, 2000 and 3000ppm product

At time zero, 1.0ml of 10 times the final required biocide concentration was added to 9.0g of the diluted pulp, so as to give the range:

50, 100, 200 and 300ppm product for PS75 and glutaraldehyde

To one 9.0g sample of diluted pulp, 1.0ml of sterile WHO water alone was added to act as a control.

All samples were then incubated at 45°C.

Total viable counts (TVCs) of surviving GAB were made on each sample after contact times of 30 minutes, 1 hour and 3 hours. In order to do this, serial dilutions were prepared from the samples by initially adding 1.0g of sample to 9.0ml EST biocide inactivating medium, mixing and allowing to stand for at least 5 minutes. Further serial dilutions were then made by removing 1.0ml and adding to 9.0ml sterile Ringers solution. From each dilution, 0.1ml was spread onto tryptone soya agar plates which were inverted and incubated at 45°C for 2 days prior to enumeration of colonies.

The above procedure for QST was repeated using pulp and water from sample 2. In this second QST, two additional samples were included in which 200ppm product of each biocide was tested. To prepare these samples, to 9.0g of chopped pulp, 1.0ml of 10 volume H_2O_2 (equating to approximately 0.3% in the pulp) was added and mixed as thoroughly as possible. 2.0g of this pulp was then added to 28g of water sample 2 and thoroughly mixed. This pulp dilution was then used for the additional samples in order to assess the potential effect of H_2O_2 on the performance of the biocides.

The results are shown in the following tables 2 to 5:

Tables 2 and 3 record TVCs in colony forming units per ml (cfu/ml) and log reductions for QSTs on diluted pulp prepared from samples 1 and 2 respectively.

Tables 4 and 5 summarise log reductions achieved by both biocides in samples 1 and 2 respectively.

Table 2: QST Results comparing TOLCIDE® PS75 to Glutaraldehyde in Sample 1

Biocide	Conc ppm product	Contact Time (Hours)					
		0.5		1.0		3.0	
		TVC in cfu/ml	Log Reduction	TVC in cfu/ml	Log Reduction	TVC in cfu/ml	Log Reduction
Control	0	4.6×10^7	-	6.7×10^7	-	8.0×10^7	-
TOLCIDE® PS75	50	1.69×10^7	0.43	1.11×10^6	1.78	1.5×10^5	2.72
	100	1.09×10^5	2.62	1.01×10^4	3.83	9.0×10^2	4.95
	200	2.8×10^5	2.21	1.7×10^3	4.60	8.0×10^2	5.00
	300	1.0×10^4	3.66	3.4×10^3	4.30	1.3×10^3	4.79
Glutaraldehyde	50	4.5×10^7	0.01	2.99×10^7	0.35	3.14×10^6	1.40
	100	1.09×10^7	0.62	1.81×10^6	1.57	1.4×10^5	2.75
	200	1.09×10^6	1.62	3.6×10^5	2.27	1.9×10^4	3.62
	300	1.03×10^5	2.65	4.1×10^4	3.22	1.0×10^3	4.90

Table 3: QST Results comparing TOLCIDE® PS75 to Glutaraldehyde in Sample 2

Biocide	Conc ppm product	Contact Time (Hours)					
		0.5		1.0		3.0	
		TVC in cfu/ml	Log Reduction	TVC in cfu/ml	Log Reduction	TVC in cfu/ml	Log Reduction
Control	0	5.3×10^7	-	2.9×10^7	-	4.3×10^7	-
TOLCIDE® PS75	50	5.1×10^6	1.01	1.9×10^6	1.18	7.0×10^5	1.78
	100	4.6×10^5	2.06	2.0×10^5	2.16	4.3×10^4	3.00
	200	1.3×10^5	2.61	3.4×10^4	2.93	2.2×10^4	3.29
	200P*	1.0×10^5	2.72	1.6×10^5	2.26	6.1×10^4	2.84
	300	1.5×10^5	2.54	5.8×10^4	2.70	3.8×10^4	3.05
Glutaraldehyde	50	4.5×10^7	0.07	3.5×10^7	0	1.85×10^7	0.36
	100	9.1×10^6	0.76	6.7×10^6	0.63	4.1×10^6	1.02
	200	2.83×10^6	1.27	1.21×10^6	1.38	2.7×10^6	1.20
	200P*	3.0×10^6	1.24	6.4×10^5	1.65	2.9×10^5	2.17
	300	1.9×10^6	1.44	1.15×10^6	1.40	8.1×10^5	1.72

* Approximately 0.3% H_2O_2 had been added to the pulp in these samples before it was diluted with water.

Table 4: Summary of Log Reductions from QSTs on Sample 1

Biocide	Conc ppm product	Contact Time (Hours)		
		0.5	1.0	3.0
		Log Reduction	Log Reduction	Log Reduction
TOLCIDE® PS75	50	0.43	1.78	2.72
	100	2.62	3.83	4.95
	200	2.21	4.60	5.00
	300	3.66	4.30	4.79
Glutaraldehyde	50	0.01	0.35	1.40
	100	0.62	1.57	2.75
	200	1.62	2.27	3.62
	300	2.65	3.22	4.90

Table 5: Summary of Log Reductions from QSTs on Sample 2

Biocide	Conc ppm product	Contact Time (Hours)		
		0.5	1.0	3.0
		Log Reduction	Log Reduction	Log Reduction
TOLCIDE® PS75	50	1.01	1.18	1.78
	100	2.06	2.16	3.00
	200	2.61	2.93	3.29
	200P*	2.72	2.26	2.84
	300	2.54	2.70	3.05
Glutaraldehyde	50	0.07	0	0.36
	100	0.76	0.63	1.02
	200	1.27	1.38	1.20
	200P*	1.24	1.65	2.17
	300	1.44	1.40	1.72

* Approximately 0.3% H_2O_2 had been added to the pulp in these samples before it was diluted with water

Results of these tests suggest that after a 1 hour 15 minute biocide contact time, THPS has reduced the population of catalase producing bacteria more effectively than glutaraldehyde. Results of both QSTs confirm this.

By looking at Tables 4 and 5, log reductions achieved by both biocides in each QST can be easily compared.

TOLCIDE® PS75 performs better against the indigenous GAB than does glutaraldehyde, particularly at the shorter contact times.

CLAIMS

1. A method of treating pulping liquors for use in the bleaching of pulp by hydrogen peroxide, said liquors containing catalase and/or catalase-producing bacteria, with a biocide which reduces or destroys said catalase and/or said bacteria, **characterised in that** said biocide comprises tris (hydroxymethyl) phosphine (THP) or a tetrakis (hydroxymethyl) phosphonium salt (THP salt).

2. A method according to Claim 1, **characterised in that** the THP salt is tetrakis (hydroxymethyl) phosphonium sulphate.

3. A method according to Claim 1, **characterised in that** the THP salt is tetrakis (hydroxymethyl) phosphonium chloride, phosphate, bromide, carbonate, acetate, citrate, formate, lactate or borate.

4. A method according to Claim 1, 2 or 3, **characterised in that** the THP or THP salt is added to the pulping liquor at a concentration of from 5ppm to 1000ppm.

5. A method according to Claim 4, **characterised in that** said concentration is from 10ppm to 200ppm.

6. A method according to Claim 4 or 5, **characterised in that** said concentration is from 15ppm to 100ppm.

7. A method according to Claim 4, 5 or 6, **characterised in that** said concentration is from 20ppm to 50ppm.

8. A method according to any one of the preceding claims, **characterised in that** the pH of the pulping liquor is from 4 to 12.

9. A method according to Claim 8, **characterised in that** the pH is from 5 to 10.

10. A method according to Claim 8 or 9, **characterised in that** the pH is from 7 to 9 in an alkaline pulping system.

11. A method according to Claim 8 or 9, **characterised in that** the pH is from 5 to 7 in an acid pulping system.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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2

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